

# Reference potential approach to the inverse Schrödinger problem: explicit demonstration of Levinson theorem and a solution scheme for Krein equation

Matti Selg

*Institute of Physics of the University of Tartu, Riia 142, 51014 Tartu, Estonia*

## Abstract

A recently proposed reference potential approach to the inverse Schrödinger problem is further developed. As previously, theoretical developments are demonstrated on example of diatomic xenon molecule in its ground electronic state. An exactly solvable reference potential for this quantum system is used, which enables to solve the related energy eigenvalue problem exactly. Moreover, the full energy dependence of the phase shift can also be calculated analytically, and as a particular result, full agreement with Levinson theorem has been achieved and explicitly demonstrated. In principle, this important spectral information can be reused to calculate an improved potential for the system, and such possibilities are discussed in the paper. Aiming at this goal, one may calculate an auxiliary potential with no bound states, whose spectral density for positive energies is exactly the same as that of the reference potential. To this end, one may solve Krein equation, which in the present context is simpler than using Gelfand-Levitan method. General solution of Krein equation can be expressed as a Neumann series. Convergence of this series of multi-dimensional integrals at distances not close to the origin is hard to achieve without a simple asymptotic formula for calculating the kernel of Krein equation. As proven in this paper, such an asymptotic formula exists, and its parameters can be easily ascertained.

## I. INTRODUCTION

Celebrated Levinson theorem [1, 2]

$$\delta_l(0) - \delta_l(\infty) = n_l\pi, \quad (1)$$

originally associated with spherically symmetric potentials in three dimensions, is simple in form, but fundamental in content. Indeed, Eq. (1) reveals a correlation between the main characteristics of the continuous and discrete energy spectra, the phase shift  $\delta_l(E)$  ( $E > 0$ ) and the total number ( $n$ ) of bound states ( $E < 0$ ). The quantity  $n_l = n + 1/2$ , if the angular momentum  $l = 0$  and a so-called half-bound state exists at  $E = 0$ , and  $n_l = n$  in any other case. As can be shown, the solution of the Schrödinger equation for  $l = 0$  and  $E = 0$  (if one exists) is not normalizable, but it still gives contribution to Levinson theorem, a half of that compared with any "normal" bound state. Therefore, the term "half-bound state" introduced by Newton [3] is fitting and illustrative for this rather special solution.

A lot of proofs of the Levinson theorem have been given by several authors using different methods (see, e.g., [4] for a brief overview), and various generalizations of Eq. (1) are known. For example, Levinson theorem has been adjusted to noncentral [3] and nonlocal [5] potentials (including bound states with  $E > 0$ ), electron-atom scattering [6], relativistic equations in one [7, 8], two [4] and more [9] dimensions, etc. In spite of the vast literature on the subject, one hardly can find any examples of calculating the full energy dependence (from 0 to  $\infty$ ) of the phase shift, which would explicitly demonstrate the Levinson theorem. Such a computation for a particular quantum system is a challenge even nowadays, but as we demonstrate below, the computational-technical difficulties can be overcome, if one is able to construct a reasonable reference potential for the system. Moreover, for any  $E > 0$ , the phase shift can be ascertained exactly, if one uses an exactly solvable reference potential. In the present context "exact solubility" means that the problem can be solved with the help of solely analytic tools, without applying methods of numerical integration.

One-dimensional inverse theory (including Levinson theorem) can be applied to diatomic molecules, since a two-particle problem can be always reduced to a one-particle problem in an effective spherically symmetric field where the angular momentum  $l$  is replaced by the rotational quantum number  $J$ . On this basis, the reference potential method developed in this paper is illustrated on example of diatomic xenon molecule ( $\text{Xe}_2$ ) in its ground

electronic state. To avoid excessive technical difficulties and concentrate on the essence of the approach, only the rotationless case ( $J = 0$ ) is analyzed.

Complete knowledge of the phase shift is one of the three obligatory preconditions for the unique solution of the inverse Schrödinger problem for a quantum system. In addition, one has to ascertain full energy spectrum of the bound states  $E_m < 0$  ( $m = 1, \dots, n$ ) and  $n$  associated real parameters  $C_m$  that uniquely fix their normalization [10]. In principle, all these data can be obtained experimentally, but unfortunately, this is almost unachievable for a real system. In this connection, one may ask: is it still possible to get some practical benefit from the rigorous methods of the inverse quantum theory? One option, as already mentioned, is to construct a reference potential based on the known data on the system's properties. Since the reference potential is fixed, all its spectral parameters are determined *a priori*. Naturally, there is no need to regain a potential which is already known by definition, but the idea is to use the calculated reference parameters as zeroth approximations to the real characteristics. Using these approximate spectral characteristics, it is possible, at least in principle, to build up a more realistic potential for the system. For example, one can construct a Bargmann potential [11, 12] whose bound states coincide with the actually observed discrete energy levels, or adjust the potential more adequately to the available scattering data. These possibilities will be discussed in this paper, which is organized as follows.

In Section II we first specify the analytic form of the reference potential, and then describe the details of calculating the phase shift for the full range of scattering states. Having ascertained the phase shift, one can calculate another important spectral characteristic, Jost function, and then fix spectral density (the terms to be specified below) for the reference potential. In Section III we demonstrate how these spectral characteristics can be reused to calculate a special auxiliary potential with no bound states, applying Krein method of solving the inverse scattering problem. Starting from this auxiliary potential, one can calculate an improved (Bargmann) potential for the system, as already mentioned. Several possibilities of this kind are discussed in Section IV. Finally, the main results of the work are summarized in Section V.

## II. FULL ENERGY DEPENDENCE OF THE PHASE SHIFT

According to the scheme outlined in the previous section, our first goal is to construct an exactly solvable (in the above specified sense) reference potential for the system. A good choice for this purpose, as explained in detail elsewhere [13, 14], is a multi-component potential composed of several smoothly joined Morse type pieces

$$V(r) = V_k + D_k [\exp(-\alpha_k(r - r_k)) - 1]^2, \quad r \in (0, \infty), \quad (2)$$

where  $V_k$ ,  $D_k$ ,  $\alpha_k$  and  $r_k$  are some constants (not definitely positive), and the subscript  $k$  corresponds to different components smoothly joined at some suitably chosen boundary points  $X_{k+1}$ . A five-component reference potential for  $\text{Xe}_2$  has been constructed [14], which is in good agreement with all known spectroscopic data. In this paper the emphasis is put on principles, not on specific details. Therefore, a more simple (but still reasonable) reference potential of three Morse components ( $k = 0, 1, 2$ ) is used. The most internal of them ( $k = 0$ ) represents a so-called pseudo-Morse potential. It means that the tiny potential well corresponding to this component (if taken separately) is just of the limit depth to completely lose the discrete energy spectrum. Consequently,  $D_0 = \hbar^2 \alpha_0^2 / (8m)$  ( $m$  being the reduced mass of the pair of atoms), so that only three independent parameters remain. The central component ( $k = 1$ ) is an ordinary Morse potential, while the most external one ( $k = 2$ ) is a "reversed" Morse potential with the parameter  $D_2$  being negative. By introducing a "reversed" component one artificially creates a potential barrier in the long-distance range. This might seem unphysical and unjustified, but the point is that the height of this artificial hump approaches zero as the parameter  $r_2$  approaches infinity. Therefore, taking a sufficiently large  $r_2$ , the hump becomes almost insignificant, while the analytic treatment remains simple and flexible. Almost equivalently, one may fix  $V(r) = 0$ , if  $r \geq r_2$ . The parameters of the reference potential are given elsewhere [15], and the curve itself is shown in Fig. 1. The described construction based on Morse type functions is not occasional. On the contrary, this is one of the very few options to easily get two linearly independent analytic solutions of the Schrödinger equation for the whole physical domain.

As already mentioned, the phase shift for the specified reference potential for any  $E \in (0, \infty)$  can be ascertained analytically. To demonstrate this, let us briefly recall the solution scheme for Morse-type potentials (see [13, 15] for more details). First one introduces dimensionless variables  $y_k = 2a_k \exp(-\alpha_k(r - r_k))$ , where the subscripts  $k = 0, 1, 2$  have

the same meaning as specified above, and  $a_k = \sqrt{2mD_k}/(\hbar\alpha_k)$ . The relevant Schrödinger equations then read

$$\frac{d^2\Psi(y_k)}{dy_k^2} + \frac{1}{y_k} \frac{d\Psi(y_k)}{dy_k} + \left[ -\frac{\mu_k^2}{y_k^2} \pm \left( \frac{a_k}{y_k} - \frac{1}{4} \right) \right] \Psi(y_k) = 0, \quad (3)$$

where the plus sign in square brackets corresponds to the subscripts  $k = 0$  and  $k = 1$ , and minus  $-$  to  $k = 2$ . The quantities  $\mu_k^2$  are defined as follows:  $\mu_k^2 = (a_k^2/D_k) \cdot (V_k + D_k - E)$ . Note that  $D_2 < 0$  and  $a_0 = 1/2$ . Next, Eq. (3) is converted to confluent hypergeometric equation, whose two linearly independent solutions can be always ascertained analytically. For example, general solution for the internal region  $r \leq X_1$  can be written as  $\Psi_0(r) = N_1\Psi_0^{(1)}(r) + N_2\Psi_0^{(2)}(r)$ , where  $\Psi_0^{(1)}(r) = A_0(y_0) \cos[B_0(y_0) - \varphi_0 - \alpha_0\mu_0r]$ ,  $\Psi_0^{(2)}(r) = A_0(y_0) \sin[B_0(y_0) - \varphi_0 - \alpha_0\mu_0r]$ , the functions  $A_0(y_0)$  and  $B_0(y_0)$  are defined as follows:

$$A_0(y_0)e^{iB_0(y_0)} \equiv \exp(-y_0/2) {}_1F_1(i\mu_0; 2i\mu_0 + 1; y_0), \quad (4)$$

and  ${}_1F_1(a; c; x)$  denotes Kummer confluent hypergeometric function. As demonstrated elsewhere [15], special solution  $\Psi_0^{(2)}(r)$  is almost insignificant if a classically forbidden region exists, i.e., if  $E < V(0)$  (note that  $V(0)$  is very large, but still finite in the framework of our approach). Correspondingly, the correct physical solution (apart from normalization) practically reduces to the particular solution  $\Psi_0^{(1)}(r)$ . Therefore, the phase parameter (NB! not yet the actual phase shift)  $\varphi_0 \equiv \alpha_0\mu_0r_0 - \arg \left[ \frac{\Gamma(2i\mu_0)}{\Gamma(i\mu_0)} \right]$  for the region  $E \lesssim V(0)$  can be calculated very easily [13, 14]:

$$\varphi_0 = \mu_0 \left( \alpha_0r_0 + 1 - \ln 2 - \frac{1}{2} \ln(1 + 4\mu_0^2) \right) + \frac{1}{2} \int_0^\infty \left( \coth t - \frac{1}{t} \right) e^{-t} \sin(2\mu_0t) \frac{dt}{t}, \quad (5)$$

where the integral can be conveniently evaluated [13]

$$I \equiv \int_0^\infty \left( \coth t - \frac{1}{t} \right) e^{-t} \sin(2\mu_0t) \frac{dt}{t} = \int_0^T e^{-t} \sin\left(\pi \frac{t}{T}\right) f(t) dt, \quad T = \frac{\pi}{2\mu_0}, \quad (6)$$

$$f(t) = \frac{\coth t - \frac{1}{t}}{t} - e^{-T} \frac{\coth(t+T) - \frac{1}{t+T}}{t+T} + e^{-2T} \frac{\coth(t+2T) - \frac{1}{t+2T}}{t+2T} - \dots$$

Another equivalent formula for this quantity reads [14]

$$I = \sum_{n=1}^\infty I_n, \quad I_n = \frac{(-1)^{n-1} 2^{2n} B_n}{(2n)(2n-1)(1+4\mu_0^2)^{2n-1}} \sum_{k=0}^{n-1} (-1)^k \binom{2n-1}{2k+1} (2\mu_0)^{2k+1}. \quad (7)$$

Here  $B_n$  denotes the  $n$ -th order Bernoulli number. Since two different definitions of the Bernoulli numbers are widely used [16] (and sometimes confused), we have to specify that the "old-style" definition is meant here, i.e.  $B_1 = 1/6$ ,  $B_2 = 1/30$ ,  $B_3 = 1/42$ , etc.

The simple scheme just described cannot be used in the region  $E \gtrsim V(0)$  where special solutions  $\Psi_0^{(1)}(r)$  and  $\Psi_0^{(2)}(r)$  become equally important. Nevertheless, the analytic treatment can be preserved. Indeed, phase shift is related to regular solutions of the Schrödinger equation, which means that the physically correct linear combination of  $\Psi_0^{(1)}(r)$  and  $\Psi_0^{(2)}(r)$  should vanish as  $r \rightarrow 0$ . From this one immediately concludes that the correct wave function  $\Psi(r) \sim \sin\{\alpha_0\mu_0 r + B_0[y_0(0)] - B_0[y_0(r)]\}$ . According to Eq. (4) it means that one first has to ascertain the argument of the complex function  ${}_1F_1[i\mu_0; 2i\mu_0 + 1; y_0(r)]$  at  $r = 0$ , to calculate the phase shift for the region  $E \gtrsim V(0)$ . This is a really complicated task, if one tries to use primary definition

$${}_1F_1(a; c; z) \equiv 1 + \frac{a}{c} \frac{z}{1!} + \frac{a(a+1)}{c(c+1)} \frac{z^2}{2!} + \dots, \quad (8)$$

because  $z \equiv y_0(0)$  is a very large quantity, and as a result, the series converges very-very slowly. It means that extremely high precision of computations is needed to get the correct result. The convergence can be essentially improved due to the relationship between the arguments,  $c = 2a + 1$ , specific to the pseudo-Morse approximation [14], namely

$$A_0(z)e^{iB_0(z)} = \sum_{n=0}^{\infty} \frac{(z/4)^{2n}}{n! (i\mu_0 + 1/2)_n} \left(1 - \frac{z/4}{i\mu_0 + 1/2 + n}\right), \quad (9)$$

where  $(a)_n \equiv \Gamma(a+n)/\Gamma(a)$  is the Pochhammer symbol. There exists even third, and in the present context, most appropriate alternative to calculate the needed quantity  $B_0(z)$ . Namely,  ${}_1F_1(a; c; z)$  can be expressed in terms of Buchholz polynomials [17]  $p_n(b, z)$ , and as has been shown [18], these polynomials in turn can be given as sums of products of polynomials in  $b$  (related to  $E$ ) and  $z$  (related to  $r$ ), separately. In the present case this leads to the formula

$$A_0(z)e^{iB_0(z)} = \sum_{n=0}^{\infty} p_n(2i\mu_0 + 1, z) \frac{{}_0F_1(; a; -z/2)}{2^n (2i\mu_0 + 1)_n}, \quad (10)$$

where  ${}_0F_1(; a; z) \equiv \sum_{n=0}^{\infty} \frac{z^n}{n! (a)_n}$ , and the Buchholz polynomials read

$$p_n(b, z) = \frac{(iz)^n}{n!} \sum_{s=0}^{[n/2]} \binom{n}{2s} f_s(b) g_{n-2s}(z), \quad (11)$$

with  $f_0(b) = 1$ ,  $f_s(b) = -(b/2 - 1) \sum_{r=0}^{s-1} \binom{2s-1}{2r} \frac{4^{s-r} B_{s-r}}{s-r} f_r(b)$ , and  $g_0(z) = 1$ ,  $g_m(z) = -\frac{iz}{4} \sum_{k=0}^{\lfloor \frac{m-1}{2} \rfloor} \binom{m-1}{2k} \frac{4^{k+1} B_{k+1}}{k+1} g_{m-2k-1}(z)$  ( $s = 1, 2, \dots$ , and  $m = 1, 2, \dots$ ). Again, as above,  $B_n$  denotes the  $n$ -th order "old-style" Bernoulli number.

Thus we have described all details of calculating the phase parameter within the pseudo-Morse approximation, which is used for  $r \in [0, X_1]$ . Having fixed this parameter, one can easily calculate the real phase shift, using the general asymptotic formula  $\Psi(r) \sim \sin[kr + \delta(k)]$  ( $k \equiv \sqrt{2mE}/\hbar$ ), and the continuity conditions for the wave function and its derivative at the boundary points  $X_{k+1}$ . The whole procedure is based on exact analytic formulae, and there is no need for numerical solution of the well-known phase equation [19]

$$\delta'(r, k) = -\frac{\sqrt{2m}V(r)}{\hbar k} \sin^2[kr + \delta(r, k)], \quad \delta(0, k) = 0, \quad (12)$$

which would be a much more difficult task, since the phase shift can only be obtained as the limit  $\delta(k) = \lim_{r \rightarrow \infty} \delta(r, k)$ . We still have to mention that it is not so easy to make a reasonable use of Eqs. (9) or (10), in order to ascertain the quantity  $B_0[y_0(0)]$ . Although convergence of these complex series is much better compared with Eq. (8), one definitely has to overcome the barrier of standard double (or fourfold) precision of high level programming languages, because much higher accuracy is actually needed. Fortunately, this is not any serious problem nowadays. Fast and powerful computational tools are freely available, such as high-precision environment UBasic [20] and an arbitrary precision library MAPM for C/C++ [21]. These tools have been used to ascertain the energy dependence shown in Fig. 2. One can see a really good agreement with the Levinson theorem, but to achieve this, the phase shift has been calculated up to very high energies (note that the energy scale in Fig. 2 is logarithmic, and it involves 20 orders of magnitude!). A good point is that there is no need for cumbersome high-precision calculations at very high energies, because this part of the curve can be accurately ascertained from general considerations. Namely, from Eq. (12), one gets  $\delta(k) = \lim_{r \rightarrow \infty} \delta(r, k) = -\frac{1}{2Ck} \int_0^\infty V(r) \{1 - \cos[2kr + 2\delta(r, k)]\} dr$  ( $C \equiv \frac{\hbar^2}{2m}$ ). Repeatedly integrating by parts and assuming  $k \rightarrow \infty$ , the following asymptotic formula can be obtained

$$\delta(k) = \frac{a_1}{k} + \frac{a_3}{k^3} + \frac{a_5}{k^5} + \dots, \quad k \rightarrow \infty, \quad (13)$$

where  $a_1 = -\frac{\int_0^\infty V(r) dr}{2C}$  and other coefficients  $a_3, a_5, \dots$  are also directly related to the

potential and its derivatives (see [15] for more details). Using Eq. (13) one can extend calculations to arbitrarily high energies, and thus, as a particular result, explicitly verify the Levinson theorem. Since the validity of Levinson theorem is beyond any doubts, Fig. 2 actually demonstrates the success of the described approach to calculating the phase shift.

It might be of interest to compare the exact phase shift with the relevant quantity obtained from a semi-classical (WKB) calculation. In the framework of the WKB approximation, the phase shift reads [22]

$$\delta(E) = \int_{r_0}^{\infty} \left[ \sqrt{\frac{E - V(r)}{C} - \frac{1}{4r^2}} - k \right] dr + \frac{\pi}{4} - kr_0, \quad (14)$$

where  $k = \sqrt{\frac{E}{C}}$  and  $r_0$  is the solution of the equation  $\frac{E - V(r)}{C} = \frac{1}{4r^2}$ . In Fig. 3 one can see a part of the exact phase curve in comparison with the WKB phase shift, calculated according to Eq. (14). As expected, semi-classical model becomes more and more reliable with increasing energy, but it fails to adequately describe the energy range  $E \lesssim V(0)$  where the exact phase can be ascertained very easily.

### III. PREPARATORY STEPS TO APPLY KREIN METHOD

How could one get any practical benefit from full knowledge of the phase shift and other spectral characteristics related to the reference potential? Trying to answer this question, let us introduce another important spectral characteristic, Jost function  $F(k) \equiv |F(k)| \exp[-i\delta(k)]$ , which fixes relationship between regular and physical solutions of the Schrödinger equation:  $\Psi(r, k) = \frac{k}{F(k)} \varphi(r, k)$ . The modulus of Jost function reads [10]

$$|F(E)| = \prod_{n=0}^N (1 - E_n/E) \exp \left[ -\frac{1}{\pi} P \int_0^{\infty} \frac{\delta(E') dE'}{E' - E} \right], \quad E \in (0, \infty). \quad (15)$$

Here  $E_n$  are the discrete energy eigenvalues and symbol  $P$  denotes the principal value of the integral. Next, we can fix spectral density

$$\frac{d\rho(E)}{dE} = \begin{cases} \pi^{-1} \sqrt{E} |F(E)|^{-2}, & E \geq 0, \\ \sum_n C_n \delta(E - E_n), & E < 0. \end{cases} \quad (16)$$

which is closely related to the real solution schemes of the inverse problem. An interesting option, among others, is to calculate an auxiliary potential  $V_0(r)$  with no bound states,



whose spectral density for  $E \geq 0$  is exactly the same as that of the reference potential ( $|F(E)|$  remains the same). We first show how this problem could be solved and then, in the next section, discuss of the usefulness of the approach for practical purposes. To calculate  $V_0(r)$ , one can apply Krein method [23, 24], based on the following integral equation:

$$\Gamma_{2r}(r') + H(r') + \int_0^{2r} \Gamma_{2r}(s)H(s - r')ds = 0 \quad (17)$$

whose kernel reads

$$H(r) \equiv \pi^{-1} \int_0^\infty \left[ \frac{1}{|F(k)|^2} - 1 \right] \cos(kr)dk. \quad (18)$$

The desired potential with no bound states then becomes [10]

$$V_0(r) = 4C \left\{ [G(x)]^2 - \frac{dG(x)}{dx} \right\}, \quad x \equiv 2r, \quad G(x) \equiv \Gamma_{2r}(2r). \quad (19)$$

Since Eq. (16) is a Fredholm integral equation of second kind, its solution can be given as a Neumann series [25]

$$\begin{aligned} G(x) = & -H(x) + \int_0^x H(x - x_1)H(x_1)dx_1 - \int_0^x \int_0^x H(x - x_2)H(x_2 - x_1)H(x_1)dx_2dx_1 + \dots \\ & + (-1)^n \int_0^x \int_0^x \dots \int_0^x H(x - x_n)H(x_n - x_{n-1}) \dots H(x_2 - x_1)H(x_1)dx_n dx_{n-1} \dots dx_1 + \dots \end{aligned} \quad (20)$$

This general formula can be easily proved, if one uses a suitable quadrature rule to discretize Eq. (17), then finds the last element of the solution vector (the only one which is actually needed) of the corresponding matrix equation, and finally goes to the limit  $h \rightarrow 0$ , where  $h$  is the step of integration. For relatively small distances the discrete analogue of Eq. (17) can be solved by Gaussian elimination [26], but with increasing  $x$  the number of equations rapidly becomes too large for this kind of approach. In this situation, one is guided to multidimensional Monte Carlo techniques using, for example, Metropolis algorithm [27]. This interesting possibility, however, is a subject for a forthcoming study and will be not further discussed here.

Calculation of Jost function and the related function  $g(k) \equiv \frac{1}{|F(k)|^2} - 1$  is described elsewhere [15, 26]. As can be seen in Fig. 4,  $g(k) = -1$  (with high accuracy) in a wide range below (and not too close) to the characteristic wave number  $k_0 = \sqrt{2mV(0)}/\hbar$ , and accurate

analytic approximations can be obtained for the remaining part of the curve. Again, as for the phase shift, a simple asymptotic formula

$$g(k) = \frac{b_1}{k^2} + \frac{b_2}{k^4} + \frac{b_3}{k^6}, \quad k \geq k_a \quad (21)$$

can be derived, where the leading coefficient  $b_1 = -\frac{V(0)}{2C}$ , and the value  $k_a = 75000 \text{ \AA}^{-1}$  has been fixed for the model system ( $\text{Xe}_2$ ) studied. Since  $H(r) = H(-r)$  is just the Fourier cosine transform of the characteristic function  $g(k)$ , calculation of this kernel in the short-distance range can be performed quite easily and accurately. As shown in Fig. 5,  $H(r)$  is a rapidly oscillating function with decaying amplitude. At longer distances, however, when the amplitude of  $H(r)$  becomes very small, even minor inaccuracies in calculating  $g(k)$  result in large relative errors of its Fourier transform. Fortunately, a correct asymptotic formula for  $H(r)$  can be fixed, namely

$$H(r) \approx a \exp(-br) \cos(\bar{k}r + \alpha), \quad r \rightarrow \infty, \quad (22)$$

where  $a, b, \bar{k}$  and  $\alpha$  are some constants to be specified. To prove Eq. (22), let us assume that  $k \rightarrow \infty$ , so that according to Eq. (21) one can approximate  $g(k) = \frac{b_1}{k^2}$ . We can perform the inverse Fourier transform  $g(k) = 2 \int_0^\infty H(r) \cos(kr) dr$ , and divide the domain into two intervals,  $(0, r_a]$  and  $[r_a, \infty)$ , where  $r_a$  is an arbitrary (but sufficiently large) quantity, such that  $\sin(kr_a) = 0$  and  $\cos(kr_a) = 1$  (these conditions can be always set, because  $k$  is arbitrary). Then, taking account of the general formula  $H'(0) = -\frac{b_1}{2} = \frac{V(0)}{4C}$  [26], integrating by parts in the first interval, and using Eq. (22) for the second interval, one comes to a relation  $H'(r_a) + ak^2 \int_{r_a}^\infty \exp(-br) \cos(\bar{k}r + \alpha) \cos(kr) dr = 0$ . It can be explicitly checked that this relation holds as  $k \rightarrow \infty$ , which completes the proof.

Since  $|F(0)|$  is an immensely large quantity [15],  $g(0) = 2 \int_0^\infty H(r) dr = -1$  (with very high precision). Let  $x$  be an arbitrary distance, such that Eq. (22) can be used to calculate  $H(x)$ . Then

$$\int_0^x H(r) dr + 1/2 = - \int_x^\infty H(r) dr = \frac{a \exp(-bx)}{\sqrt{b^2 + \bar{k}^2}} \cos(\bar{k}x + \alpha + \beta), \quad (23)$$

where  $\cos \alpha = \frac{b}{\sqrt{b^2 + \bar{k}^2}}$  and  $\sin \alpha = \frac{\bar{k}}{\sqrt{b^2 + \bar{k}^2}}$ . Thereafter, accurately evaluating the integral  $\int_0^x H(r) dr$ , the desired parameters can be easily fixed by direct least-squares fit of Eq. (23).

To be more specific, Simpson rule with integration step  $h = 10^{-7}$  Å was used for  $x = 0.038$  Å, and as a result, the following set of parameters has been ascertained:  $a = 2.7125$  1/Å,  $b = 70.04656$  1/Å,  $\alpha = -3.67004$ , and most importantly,  $\bar{k} = 19165.07$  1/Å  $\approx 0.99866$   $k_0$ . Fig. 6 demonstrates how nicely Eq. (22) already works at  $r \gtrsim 0.03$  Å. Thus, for this region there is no need for troublesome Fourier transform to calculate the kernel of the Krein equation, which makes Eq. (20) much more useful for practical purposes.

#### IV. IMPROVING THE INITIAL POTENTIAL

Having ascertained all spectral characteristics of the reference potential and described a possible solution scheme of the Krein equation, one cannot ignore the principle question: what is the practical point of all this? Can these data be used to calculate an improved potential for the system? First, we have to point out that such an improved (in some sense) potential  $V_1(r)$  can be ascertained without auxiliary calculations described in Section III. Most easily this can be demonstrated in the frame of Gelfand-Levitan method [28], which is based on the integral equation

$$K(r, r') + G(r, r') + \int_0^r K(r, s)G(s, r')ds = 0, \quad (24)$$

whose kernel can be directly linked with the reference potential  $V(r)$

$$G(r, r') = \int_{-\infty}^{\infty} [d\rho^{(1)}(E) - d\rho^{(0)}(E)] \varphi(r, E)\varphi(r', E). \quad (25)$$

Here

$$\frac{d\rho^{(1)}(E) - d\rho^{(0)}(E)}{dE} = \begin{cases} \pi^{-1}\sqrt{E} \left[ |F^{(1)}(E)|^{-2} - |F(E)|^{-2} \right], & E \geq 0, \\ \sum_k C_k^{(1)} \delta(E - E_k^{(1)}) - \sum_m C_m^{(0)} \delta(E - E_m^{(0)}), & E < 0, \end{cases} \quad (26)$$

the regular solution  $\varphi(r, E)$  as well as the quantities  $\rho^{(0)}(E)$ ,  $|F^{(0)}(E)|$ ,  $E_m^{(0)}$  and  $C_m^{(0)}$ , ( $m = 1, 2, \dots, n$ ) correspond to the reference potential  $V(r)$ , while  $d\rho^{(1)}(E)$ ,  $|F^{(1)}(E)|$ ,  $E_k^{(1)}$  and  $C_k^{(1)}$  ( $k = 1, 2, \dots, l$ ) are related to  $V_1(r)$ . Suppose we are looking for a potential  $V_1(r)$  whose spectral density at  $E \geq 0$  is exactly the same as that for the reference potential  $V(r)$ , i.e.,  $|F^{(1)}(E)| = |F(E)|$ , but the discrete energy spectrum and the related norming

constants are different. In this case the kernel is separable:

$$G(r, r') = \sum_k C_k^{(1)} \varphi(r, E_k^{(1)}) \varphi(r', E_k^{(1)}) - \sum_m C_m^{(0)} \varphi(r, E_m^{(0)}) \varphi(r', E_m^{(0)}), \quad (27)$$

and Eq. (24) can be easily solved. Thus, in principle, one can directly calculate the difference of the two potentials in question (see, e.g., [10] for more details)

$$V_1(r) - V(r) = 2C \frac{d}{dr} K(r, r) = -2C \left\{ \ln [\det S^{(n+l)}(r)] \right\}'', \quad (28)$$

where the  $(n+l) \times (n+l)$  matrix  $S^{(n+l)}(r) \equiv I + \int_0^r R^{(n+l)}(s) ds$ ,  $I$  is the corresponding unit matrix, and the elements of another matrix  $R^{(n+l)}(s)$  read

$$R_{jk}^{(n+l)}(s) = C_j \varphi(s, E_j) \varphi(s, E_k), \quad (j, k = 1, 2, \dots, n+l). \quad (29)$$

The quantities  $C_j$  and  $E_j$  are defined as follows:  $C_j \equiv C_j^{(1)}$ , and  $E_j \equiv E_j^{(1)}$ , if  $1 \leq j \leq l$ ;  $C_j \equiv -C_{j-l}^{(0)}$ , and  $E_j \equiv E_{j-l}^{(0)}$ , if  $l < j \leq n+l$ . If the parameters  $E_j^{(1)}$  and  $C_j^{(1)}$  are taken equal to the actually observed values of these quantities, the potential  $V_1(r)$  can be considered more realistic than the reference potential  $V(r)$ .

According to Eqs. (28) and (29), one only has to accurately evaluate the regular solutions  $\varphi(s, E_j)$  ( $j = 1, 2, \dots, n+l$ ), in order to ascertain the improved potential  $V_1(r)$ , which seems to essentially reduce the computation time. This imagination, however, is deceptive, because full knowledge (from 0 to  $\infty$ ) of  $n+l$  regular solutions is in fact equivalent to calculating  $n+l$  auxiliary potentials for the system. Indeed, let us recall that once the ground state wave function  $\Psi_0(r)$  (or any other bound state wave function) is known, the potential  $U(r)$  is immediately known as well (up to a constant) [29]. This general rule directly results from the Schrödinger equation, if one takes the ground state energy as the zero point of the energy scale:  $U(r) = C \Psi_0''(r)/\Psi_0(r)$ . In the present case we have to take into consideration that the solutions  $\varphi(r, E_j^{(1)})$  are not the real eigenfunctions, if  $E_j^{(1)} \neq E_j^{(0)}$ . Nevertheless, since the norming constants  $C_j^{(1)}$  are expected to be known, the regular eigenfunctions  $\varphi_1(r, E_j^{(1)})$  related to the potential  $V_1(r)$  can be easily ascertained using the well-known relations of the quantum inverse theory [10]. For example, if there was only one bound state with energy  $E_1^{(1)}$  and norming constant  $C_1^{(1)}$ , then  $\varphi_1(r, E_1^{(1)}) = \varphi(r, E_1^{(1)}) \left[ 1 + C_1^{(1)} \int_0^r \varphi^2(s, E_1^{(1)}) ds \right]^{-1}$ . Thus, seemingly simple Eq. (28) "hiddenly" contains a procedure of removing all previous bound states (equivalent to calculating regular eigenfunctions  $\varphi(r, E_j^{(0)})$ ,  $j = 1, 2, \dots, n$ ),

and introducing new bound states (equivalent to calculating regular solutions  $\varphi(r, E_j^{(0)})$ ,  $j = 1, 2, \dots, l$ ) related to the improved potential  $V_1(r)$ .

The explicit procedure equivalent to Eq. (28) can be performed as follows [30, 31]. Starting from the potential  $V_n(r) \equiv V(r)$ , one first removes its zeroth level  $E_0$  and calculates a new potential, isospectral with the initial one (apart from  $E_0$ )

$$V_{n-1}(r) = V_n(r) + 2C \left\{ \frac{2\Psi_0^{(n)}(r) \left( \Psi_0^{(n)}(r) \right)'}{\int_r^\infty \left( \Psi_0^{(n)}(s) \right)^2 ds} + \left[ \frac{\left( \Psi_0^{(n)}(r) \right)^2}{\int_r^\infty \left( \Psi_0^{(n)}(s) \right)^2 ds} \right]^2 \right\}. \quad (30)$$

Here  $\Psi_0^{(n)}(r)$  is the eigenfunction of the zeroth level, not necessarily normalized (note that the norming constant is absent here). The new set of wave functions for  $V_{n-1}(r)$  can also be expressed in terms of the previous wave functions for  $V_n(r)$  [31]. The procedure can be continued, i.e., one can remove, one by one, all bound states along with calculating new auxiliary potentials at each step, until he finally comes to the potential  $V_0(r)$  with no bound states. Thereafter, one can introduce new bound states  $E_j^{(1)}$  with norming constants  $C_j^{(1)}$  in exactly the same way as described above, i.e.,

$$V_1(r) - V_0(r) = -2C \left\{ \ln [\det S^{(l)}(r)] \right\}'' , \quad (31)$$

where the  $l \times l$  matrix  $S^{(l)}(r) \equiv I + \int_0^r R^{(l)}(s) ds$ , and

$$R_{jk}^{(l)}(s) = C_j^{(1)} \varphi(s, E_j^{(1)}) \varphi(s, E_k^{(1)}), \quad (j, k = 1, 2, \dots, l). \quad (32)$$

Alternatively, one can solve Krein equation, as described in Section III, and then use Eq. (19) to get the auxiliary potential  $V_0(r)$  with no bound states. As mentioned, all three approaches to calculating the improved potential  $V_1(r)$  are equivalent, in presumption that the modulus of Jost function remains unchanged, which means that [10]

$$F_1(k) = \prod_{j=1}^l \left( \frac{k - ik_j^{(1)}}{k - ik_j^{(0)}} \right) \cdot F_0(k), \quad (33)$$

and

$$F(k) = \prod_{j=1}^n \left( \frac{k - ik_j^{(0)}}{k - ik_j^{(1)}} \right) \cdot F_0(k), \quad (34)$$

where  $F_1(k)$ ,  $F(k)$  and  $F_0(k)$  are the Jost functions for the potentials  $V_1(r)$ ,  $V(r)$  and  $V_0(r)$ , respectively,  $k_j^{(1)} = \sqrt{2mE_j^{(1)}/\hbar}$  and  $k_j^{(0)} = \sqrt{2mE_j^{(0)}/\hbar}$ .

An alternative to applying Eq. (31) is to introduce new bound states step-by-step, starting from the auxiliary potential  $V_0(r)$ . This well-known procedure is based on the formula [10] (see also [26])

$$V_k(r) = V_{k-1}(r) - 2C \left\{ \ln \left[ 1 + C_k^{(1)} \int_0^r \varphi_{k-1}^2(s, E_k^{(1)}) ds \right] \right\}'' , \quad (k = 1, 2, \dots, l) \quad (35)$$

where the regular solution  $\varphi_{k-1}(s, E_k^{(1)})$  is not the real eigenfunction, since it is related to the potential  $V_{k-1}(r)$ . Naturally, the norming constants  $C_j^{(1)}$  in Eqs. (29), (32) and (35) are different (although the same notation is used), because they are related to different potentials.

Currently, one can only guess which of the described approaches is computationally most effective. However, one cannot argue that solution of Krein equation is an interesting problem on its own, and the scheme outlined in Section III is realizable. At least, it seems reasonable to first calculate the auxiliary potential  $V_0(r)$  with no bound states, and then try to improve the initial potential. Introducing "real" bound states is not the only option in this context. For example, one can construct another potential  $\bar{V}_0(r)$  with no bound states, a Bargmann potential whose Jost function reads

$$\bar{F}_0(k) = \prod_{j=1}^m \left( \frac{k + ia_j}{k + ib_j} \right) \cdot F_0(k), \quad (36)$$

where the quantities  $a_j \neq b_j$  are real and positive. For simplicity, let us assume that  $m = 1$  ( $a_1 \equiv a$  and  $b_1 \equiv b$ ). Then [10]

$$\bar{V}_0(r) - V_0(r) = -2C \left\{ \ln \frac{W[f_1(r, ia), \varphi_1(r, ib)]}{b^2 - a^2} \right\}'' , \quad (37)$$

where the symbol  $W$  denotes Wronskian determinant, and  $f_1(ia, r)$  is the Jost solution of the Schrödinger equation ( $f_1(r, ia) \rightarrow \exp(-ar)$  as  $r \rightarrow \infty$ ). Both  $f_1(r, ia)$  and the regular solution  $\varphi_1(r, ib)$  are related to the potential  $V_0(r)$ . Thus, suitably choosing the parameters  $a_j$  and  $b_j$ , one can, in principle, take a more adequate account of the scattering data or of the known behavior of the potential near the origin. Suppose, for example, that the quantity  $\bar{V}_0(0)$  is known. Then, using the formula

$$\frac{d}{dr} \left[ \frac{W[f_1(r, ia), \varphi_1(r, ib)]}{b^2 - a^2} \right] = -f_1(r, ia), \varphi_1(r, ib), \quad (38)$$

which is valid for any two solutions of the Schrödinger equation for the same potential, taking account that  $|F_0(k)|^2 = 1 + \frac{V(0)}{2Ck^2} + 0(k^{-4})$  [15], and consequently,  $|\bar{F}_0(k)|^2 = 1 + \frac{\bar{V}(0)}{2Ck^2} + 0(k^{-4})$ , one comes to a more transparent form of Eq. (37):

$$\frac{\bar{V}_0(r) - V_0(r)}{\bar{V}_0(0) - V_0(0)} = \frac{d}{dr} \left[ \frac{f_1(r, ia), \varphi_1(r, ib)}{W[f_1(r, ia), \varphi_1(r, ib)]} \right]. \quad (39)$$

One can easily check that the right side of Eq. (39) indeed approaches unity as  $r \rightarrow 0$ , because  $\varphi_1(0, ib) = 0$ , but  $f_1(0, ia) \neq 0$  (otherwise  $E_a = -Ca^2$  would be a bound state).

Using the modified auxiliary potential  $\bar{V}_0(r)$ , one can construct another improved potential for the system, introducing new bound states all at once, according to Eq. (31) or step-by-step, according to Eq. (35).

## V. CONCLUSION

Starting from a known reference potential, one can calculate important spectral characteristics of the quantum system, which are almost unattainable in a real experiment. Then it is possible, in principle, to construct another, in some sense more realistic potential for the system. This kind of approach has been applied to diatomic xenon molecule in its ground electronic state. The phase shift for the full range of scattering states has been calculated, and excellent agreement with Levinson theorem explicitly demonstrated. All this important spectral information, along with full discrete energy spectrum, can be stored into Jost function, and then reused for constructing a new (possibly improved) potential.

Choice of a proper reference potential, applicable in the whole physical domain, is a difficult and rather speculative task in any particular case. A variety of semiclassical schemes have been devised to deduce the potential directly from the available experimental data, and these concepts are constantly improved and developed (see, e.g., [32, 33]). Such methods, although inaccurate from the rigorous quantum mechanical point of view, have proven useful for practical purposes. Therefore, they might help to construct a reference potential, which can be used as a reasonable approximation to the real potential. Only if the reference potential is realistic enough, there is a chance to construct a Bargmann potential that would be even more realistic. On the other hand, as demonstrated in this paper, the computational-technical difficulties can be overcome much more easily, if one chooses an exactly solvable reference potential (in the sense specified in Section I). To this end, a multi-component

potential of smoothly joined Morse-type pieces is especially suitable. Full energy dependence of the phase shift for such a potential can be ascertained analytically, using a method (described in Section II), which is largely based on a so-called pseudo-Morse approximation for the small distances (and high energies) region of the potential. In this paper, only a single pseudo-Morse component has been used for the range  $r \in [0, X_1]$ . As demonstrated elsewhere [13, 14], adding more pseudo-Morse components does not bring along any serious computational problems, so one can include just as many components of this type as he considers reasonable.

An important constituent of the overall concept is Krein method for calculating an auxiliary potential  $V_0(r)$  with no bound states. For this purpose one uses the Jost function, which has been ascertained for the reference potential. General solution of Krein equation, Eq. (20), can be given as a series of multi-dimensional integrals (Neumann series). Thus, Eq. (20) represents a formulation of a serious (but very interesting) computational-technical problem, not solved yet. Fortunately, a simple asymptotic formula, Eq. (22), for the kernel of Krein equation can be used to accurately evaluate the multi-dimensional integrands in Eq. (20). As demonstrated in Section III, Eq. (22) can already be used at rather small distances,  $r \gtrsim 0.03 \text{ \AA}$ , instead of performing Fourier cosine transform of the characteristic function  $g(k)$  there.

We discussed several possibilities of improving the initial reference potential in the rigorous framework of the quantum-mechanical inverse theory. In particular, explicit calculation of the auxiliary potential  $V_0(r)$  is not obligatory for this purpose, if one prefers to calculate regular eigenfunctions of all bound states for the whole physical domain, and additionally assumes that  $|F^{(1)}(E)| = |F(E)| = |F_0(E)|$  (see Eqs. (33), (34) and the paragraph between Eqs. (26) and (27)). In this case, one can try to use Eqs. (28) and (29) to ascertain an improved potential  $V_1(r)$  whose discrete energy spectrum would exactly coincide with the "real" one. This method is extremely difficult to implement, but exactly the same can be said about other possible approaches described and discussed in Section IV. None of these schemes has been realized yet, and there is no real ground to give preference to any of them. In this paper the emphasis has been put on promoting Krein method to calculating the auxiliary potential with no bound states, which is an interesting theoretical and computational-technical problem on its own. Rapid development of parallel computing and Grid technology opens a new powerful channel for the solution of such complex problems,



which suggest optimism for further research in this direction.

### Acknowledgement

The research described in this paper has been supported by Grants No 5863 and 5549 from the Estonian Science Foundation.

- 
- [1] N. Levinson, K. Danske Vidensk. Selsk. Mat-fys. Medd. **25**, 9 (1949).
  - [2] N. Levinson, Mat. Tidsskr. B **13**, 25 (1949).
  - [3] R. G. Newton, Scattering Theory of Waves and Particles, 2nd ed. (Springer-Verlag, New York, 1982).
  - [4] Shi-Hai Dong, Xi-Wen Hou, and Zhong-Qi Ma, Phys. Rev. A **59**, 995 (1999).
  - [5] A. Martin, Nuovo Cimento **7**, 607 (1958).
  - [6] L. Rosenberg and L. Spruch, Phys. Rev. A **54**, 4985 (1996).
  - [7] Qiong-gui Lin, Eur. Phys. J. D **7**, 515 (1999).
  - [8] S.-H. Dong, Eur. Phys. J. D **11**, 159 (1999).
  - [9] Yu Jiang, Phys. Rev. A **71**, 022714 (2005).
  - [10] K. Chadán and P. C. Sabatier, Inverse Problems in Quantum Scattering Theory, 2nd ed. (Springer-Verlag, New York, 1989).
  - [11] V. Bargmann, Phys. Rev. **75**, 301 (1949).
  - [12] V. Bargmann, Rev. Mod. Phys. **21**, 488 (1949).
  - [13] M. Selg, Phys. Rev. E **64**, 056701 (2001).
  - [14] M. Selg, J. Mol. Spectrosc. **220**, 187 (2003).
  - [15] M. Selg, arXiv:quant-ph/0506064 v1 (8 Jun 2005).
  - [16] <http://mathworld.wolfram.com/BernoulliNumber.html>.
  - [17] H. Buchholz, The Confluent Hypergeometric Function (Springer-Verlag, Heidelberg, 1969).
  - [18] J. Abad and J. Sesma, The Mathematica Journal **5**, 74 (1995).
  - [19] Philip M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933).
  - [20] <http://www.rkmath.rikkyo.ac.jp/~kida/ubasic.htm>.
  - [21] <http://www.tc.umn.edu/~ringx004/mapm-main.html>.

- [22] L. D. Landau and E. M. Lifshitz, Quantum Mechanics-Nonrelativistic Theory (Pergamon, 1976).
- [23] M. G. Krein, Dokl. Akad. Nauk SSSR **88**, 405 (1953).
- [24] M. G. Krein, Dokl. Akad. Nauk SSSR **111**, 1167 (1956).
- [25] Eric W. Weisstein. "Integral Equation Neumann Series." From MathWorld—A Wolfram Web Resource: <http://mathworld.wolfram.com/IntegralEquationNeumannSeries.html>.
- [26] M. Selg, arXiv:quant-ph/0506130 v1 (16 Jun 2005).
- [27] N. Metropolis, A. Rosenbluth, A. Rosenbluth, A. Teher, and E. Teher, J. Chem. Phys. **21**, 1087 (1953).
- [28] I. M. Gel'fand and B. M. Levitan, Izv. Akad. Nauk SSSR. Ser. Mat. **15**, 309 (1951) [Am. Math. Soc. Transl. (ser. 2) **1**, 253 (1955)].
- [29] F. Cooper, A. Khare, and U. Sukhatme, Phys. Rep. **251**, 267 (1995)
- [30] P. B. Abraham and H. E. Moses, Phys. Rev. A **22**, 1333 (1980).
- [31] Marshall Luban and D. L. Pursey, Phys. Rev. D **33**, 431 (1986).
- [32] Photos G. Hajigeorgioua and Robert J. Le Roy, J. Chem. Phys. **112**, 3949-3957 (2000).
- [33] Jenning Y. Seto, Robert J. Le Roy, Jean Vergès and Claude Amiot, J. Chem. Phys. **113**, 3067-3076 (2000).

## Figure captions

Fig. 1. Three-component model potential for the system ( $\text{Xe}_2$  in ground electronic state) investigated. All components have the well-known analytic form of the Morse potential, but the ordinary Morse approximation is used only in the central range  $r \in [X_1, X_2]$  (see the explanations in Section II). The parameters of the components as well as the calculated discrete energy levels (24 in total) are given in Ref. 15.

Fig. 2. Explicit demonstration of the Levinson theorem ( $\delta(0) - \delta(\infty) = n\pi$ ) for the model system studied. As needed,  $\delta(0) = 24\pi$ , since the system has 24 bound states. At  $E = 3.146294$  meV, the phase shift passes a zero, and then remains negative, very slowly approaching the limit ( $\delta(\infty) = 0$ ) as  $E \rightarrow \infty$ . The left side-inset shows the nearly linear energy dependence as  $E \rightarrow 0$ , in full agreement with general-theoretical concepts. In the right-side inset one can see that the phase curve has an inflection point near  $E = V(0)$ .

Fig. 3. A comparison between the exact phase shift (solid line) and WKB phase shift (open circles), calculated according to Eq. (14). The difference between the two phase curves is shown in the inset.

Fig. 4. Visualization of the characteristic function  $g(k) = |F(k)|^{-2} - 1$ , which determines the kernel of the Krein equation. As can be seen,  $g(k) = -1$  (with very high precision) if  $k \lesssim k_0 = \sqrt{2mV(0)}/\hbar$ , then starts to monotonously decrease, and  $g(k) \rightarrow 0$  as  $k \rightarrow \infty$ . In spite of the seeming simplicity of the energy dependence, the whole curve has to be calculated very accurately up to high energies, in order to accurately ascertain the kernel  $H(r)$ . The high-energy part of the curve ( $k \geq k_a$ ) has been calculated according to Eq. (21). The asymptotic wave number  $\bar{k}$  (see Eq. (22)) is also shown.

Fig. 5. Demonstration of the behavior of Krein  $H$ -function (kernel of Krein equation) given by Eq. (18). The lower graphs start where the upper ones end. Note that the period of oscillations rapidly achieves the characteristic value  $\frac{2\pi}{\bar{k}}$ .

Fig. 6. Demonstration of the validity of the asymptotic formula for calculating the kernel of Krein equation. Open circles in the figure represent the result of Fourier cosine transform according to Eq. (18), while the solid line corresponds to Eq. (22). One can

see excellent agreement between the two principally different approaches to calculating the same quantity.













